

Effect of CdTe thickness reduction in high efficiency CdS/CdTe solar cells

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ABSTRACT

High efficiency CdTe solar cells are typically grown with CdTe thicknesses from 3 to 15 μm , although the thickness required for 90% absorption of the incident irradiation at 800 nm is only $\sim 1 \mu\text{m}$. In this paper, we present the effect of CdTe thickness reduction on the performance of CdS/CdTe solar cells in which both the CdS and CdTe films were grown by sputtering. We produced a series of cells with different CdTe thickness (from 0.5 to 3.0 μm), and held the CdS thickness and back-contact-processing constant. The effect of CdTe thickness reduction on the diffusion of CdS into CdTe was studied using optical absorption and x-ray diffraction techniques. Only slight decreases occur in open-circuit voltage, short-circuit current, and fill factor with decrease in CdTe film thickness to 1.0 μm . Almost 10% efficient cells were obtained with 1 μm CdTe. Below 1 μm , all cell parameters decrease more rapidly, including the red quantum efficiency.

INTRODUCTION

CdS/CdTe solar cells prepared by high-temperature processes such as vapor transport deposition[1] or closed-space sublimation,[2,3] typically are fabricated with CdTe thicknesses ranging from 3 to 15 μm . By contrast, cells fabricated by low temperature processes such as magnetron sputtering[4] or electrodeposition,[5] are typically fabricated with CdTe thicknesses from 1.5 to 2.5 μm . It is well-known that the optical absorption coefficient in CdTe is high enough that nearly full absorption of light below $\sim 800 \text{ nm}$ should occur for thicknesses above 1 μm . Low-temperature-fabricated cells have smaller grain sizes ($\sim 0.5\text{--}1 \mu\text{m}$) than the thicker, high-temperature films ($\sim 1\text{--}5 \mu\text{m}$). Cells fabricated with the thicker CdTe films are often prepared with the use of more aggressive chemical etching prior to the application of the back contact. It has been suggested that grain boundary properties may be sufficiently different for the large grain film to explain the apparent need to have thicker films to avoid shunts.

In order to determine some of the factors which affect the thickness dependence of cell performance, we have fabricated a series of CdS/CdTe cells by magnetron sputtering with all the fabrication parameters held constant except for the CdTe thickness. Thus, we have prepared cells with CdTe layer thickness from 0.5 μm to 3.0 μm .

Recently, considerable attention has also focused on the possible role of CdTe thickness in the long-term stability of CdTe cells prepared with contacts having copper which can diffuse deep into the CdTe and even reach the CdS/CdTe junction.[6] Thus, in addition to studies of the performance immediately after fabrication, we have also performed some limited stressing of the cells to test whether the thin CdTe cells have poorer stability under one-sun light soaking at open-circuit voltage.

EXPERIMENTAL

The magnetron sputtered cells were prepared as described in detail previously.[4] Essential features included the use of $8\ \Omega/\text{cm}$ $\text{SnO}_2\text{:F}$ -coated soda-lime glass superstrates from Pilkington, Plc, rf magnetron sputtering of $0.13\ \mu\text{m}$ CdS followed by magnetron sputtering of the CdTe layer with seven different thicknesses from $0.5\ \mu\text{m}$ to $3.0\ \mu\text{m}$. Sputtering was done at $250\ ^\circ\text{C}$. After vapor CdCl_2 treatment at $387\ ^\circ\text{C}$ and back-contact evaporation of $3\ \text{nm}$ Cu and $20\ \text{nm}$ Au, the cells were diffused at $150\ ^\circ\text{C}$ for 45 minutes in air. The back-contact metals were evaporated through a mask which defined typically nine cells of area $0.116\ \text{cm}^2$ on each substrate. No further wet processing was done after the initial superstrate cleaning in hot water with an alkaline soap. No adjustments were made in either the CdCl_2 treatment or the back-contact processing to accommodate the thinner CdTe. Thus it is possible that, since these steps were optimized for cells with $2.3\ \mu\text{m}$ CdTe, some adjustment of these steps might result in higher efficiency for either thicker or thinner cells.

Cells were measured initially within one day after back-contact diffusion. Some cells of each thickness were stressed at open circuit under a metal-halide stadium lamp at approximately $55\ ^\circ\text{C}$ in air. After stressing, the cells happened to be stored in room light at ambient for several weeks before the second I-V measurements. Current-voltage measurements were obtained with a Keithley model 2400 Source Meter and illumination with a 1000 watt Oriel solar simulator filtered for air mass 1.5 illumination. Spectral-quantum-efficiency measurements were performed with no light bias using an ELH tungsten-halogen lamp and a monochromator. Optical transmission was measured through the cells between the copper/gold contacts using a Varian model 300 double beam spectrometer. X-ray diffraction was measured on a Scintag model XDS2000 powder diffractometer. Results are presented for the $\langle 531 \rangle$ reflection which has improved resolution and less alignment sensitivity than lower-order reflections. Full scans show the crystallographic orientation of the CdTe is not sensitive to the CdTe thickness. The magnetron-sputtered CdTe as-deposited is strongly $\langle 111 \rangle$ oriented but after CdCl_2 treatment, the resulting CdTe grains are almost randomly oriented.

OPTICAL TRANSMISSION AND X-RAY DIFFRACTION

The room temperature optical transmission of the cell structures (without back contact) clearly show the band edge of CdTe at about $830\ \text{nm}$ and the thinner cells also show the beginning of significant light transmission in the red. At $800\ \text{nm}$, the $0.5\ \mu\text{m}$ cell transmits 28% (the $0.75\ \mu\text{m}$ cell 17%) and at $600\ \text{nm}$ the transmission is 5%. X-ray diffraction from the film side near $2\theta = 90^\circ$ shows the presence of a $\text{CdS}_x\text{Te}_{1-x}$ alloy, which is expected to be formed at the CdS/CdTe interface. (See Fig. 1.) McCandless, *et al.*, [7] and Mao, *et al.*, [8] have shown that alloying can be studied conveniently at the higher order reflections. We have chosen to use the $\langle 531 \rangle$ near 90° . The K_α peak for pure CdTe occurs at 89.25° . However, alloying with S produces material with a smaller lattice constant depending on the amount of S present in the alloy. Fig. 1 shows clearly the strong peak from CdTe at 89.25° and also a broader band due to the alloy which appears to be centered near 89.8° , especially evident for the $0.5\ \mu\text{m}$ thick CdTe cell. The cell used for the $2.5\ \mu\text{m}$ of CdTe was a control sample fabricated without the CdS layer. This trace shows, therefore, no CdS_xTe_{1-x} alloy band. Some penetration of the x-rays to the junction region occurs so the corresponding trace shows a weak peak at 90.2° which is from the $\text{SnO}_2\text{:F}$ -coated glass substrate. However for samples with thinner CdTe layers, the alloy band increases in intensity, due to the greater penetration of the x-rays into the interface (junction) region. It is remarkable that for $0.75\ \mu\text{m}$ of CdTe the pure CdTe $\langle 531 \rangle$ peak is very weak and

shifted slightly by about 0.1° . It is essentially gone for the samples prepared with $0.5\ \mu\text{m}$ CdTe. Instead the alloy band centered near 89.8° is the strongest for the thinnest CdTe indicating that essentially all of the original CdTe layer has been consumed in the process of alloying.

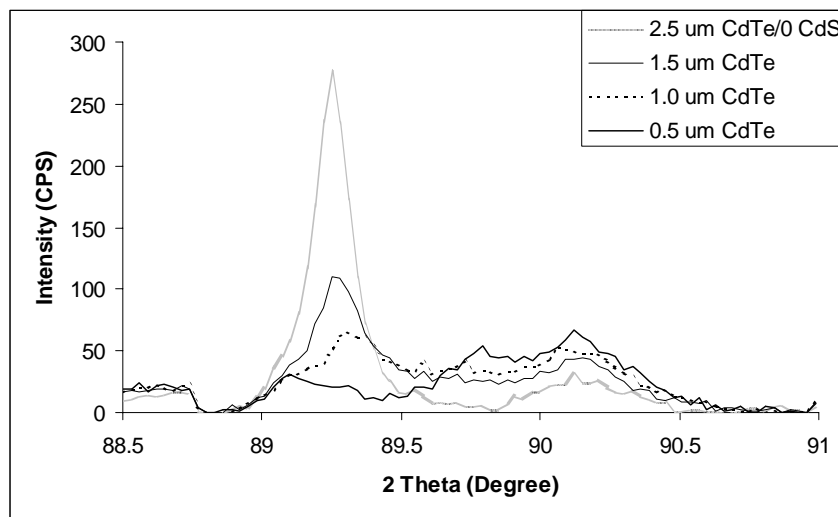


Fig. 1. X-ray diffractogram of complete cell structures except for back contact. Peak at 89.25° is pure CdTe, at 90.2° is SnO_2 and the CdSTe alloy extends between.

An x-ray peak at 89.8° is representative of $\text{CdS}_x\text{Te}_{1-x}$ with $x=0.06$. As shown in refs. 7 and 8, the alloy peak in CdS/CdTe cells is relatively broad indicating that there is a range of alloy compositions formed. The width of the band is consistent with alloy x -values in the range $0 \leq x \leq 0.06$. The presence of this Te-rich alloy is confirmed in the quantum efficiency measurements on these cells. (See below.) In addition, there is evidence from QE measurements of a S-rich alloy as well, although we have not seen it clearly in x-ray diffraction.

QUANTUM EFFICIENCY

The external quantum efficiency of the seven different thickness cells are quite similar, as seen from Fig. 2. All show the characteristic shift of the QE edge deeper into the near infrared which results from slight alloying of the CdTe with S. Large band bowing in the alloy $\text{CdS}_x\text{Te}_{1-x}$ leads to decreasing band gap up to $x = 0.2$. [9] The rounded shape of the QE in the region from 520 to 590 nm is characteristic of the formation of the S-rich alloy $\text{CdS}_x\text{Te}_{1-x}$ with $x \leq 0.97$. Presumably the S-rich alloy exhibits very poor carrier collection, similar to the pure CdS, so that the QE is decreased by the amount of the absorption in this alloyed layer. With this assumption we can estimate the thickness of this S-rich alloy to be no more than $0.05\ \mu\text{m}$. Finally, the QE in the range from 420 to 500 nm permits an estimate the thickness of the pure CdS remaining in these cells. The residual CdS thickness is quite constant in these cells at $\sim 0.09\ \mu\text{m}$.

Essentially the only dependence on CdTe thickness down to $0.75\ \mu\text{m}$ evident from the quantum efficiency is a gradual decrease in collection across the spectrum (400-900 nm). This could be evidence for gradually decreasing junction quality and might be improved by adjustments to the CdCl_2 annealing step. For $0.5\ \mu\text{m}$ the red QE droop clearly reflects incomplete absorption and a spectrum-wide drop in current indicates that the junction is

degraded for this thinnest CdTe cell. From the x-ray diffraction evidence, this thinnest cell also has essentially no pure CdTe remaining and this could play a significant role in the poor performance. Methods to reduce interdiffusion, such as preannealing the CdS before deposition of CdTe, or the use of a high resistivity transparent conductor between the heavily doped SnO₂:F and the CdS or CdTe, might improve the performance of the thin CdTe cells significantly.

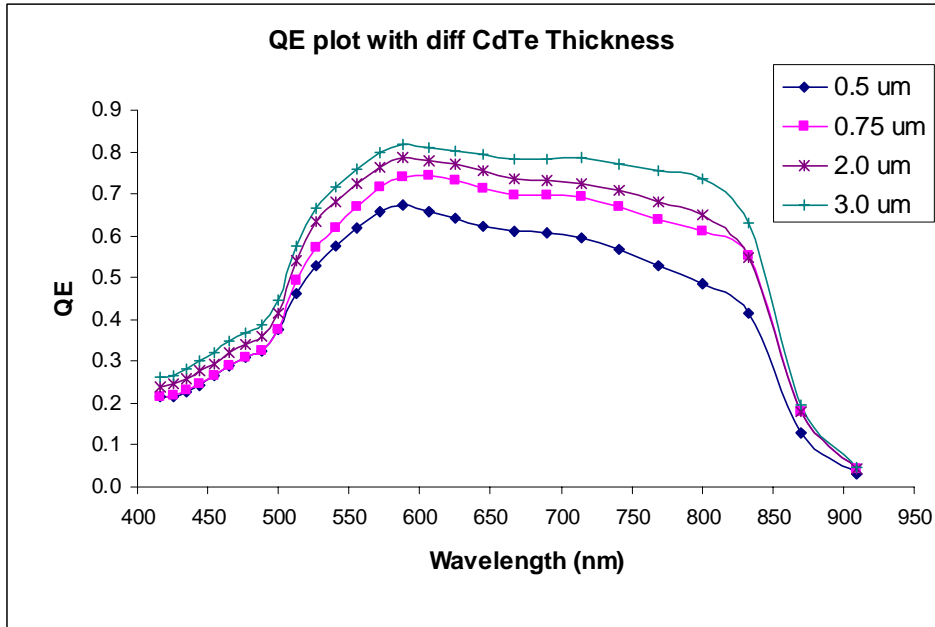


Fig. 2. Quantum efficiencies for cells with four different CdTe thicknesses as shown in legend.

I-V CURVES AND CELL EFFICIENCY

Similar to the behavior of the QE, the electrical parameters of the cells exhibited only a gradual decrease in performance as the CdTe thickness decreased to 0.75 μm, but then a substantial decrease occurs for 0.5 μm CdTe. The data for the average of the three best cells of each plate are collected in the four panels of Fig. 3. Initial values and values after seven days of stress in air at ~55 °C, one-sun illumination, and open-circuit voltage are shown. The initial V_{OC} remains above 730 mV even for 0.75 μm of CdTe. J_{SC} values remain high down to 1.5 μm. Initial fill factors remain well above 60% even for 0.75 μm. Similarly these factors combine to yield efficiencies which trend lower but remain above 9% for 0.75 μm. Only the cells with the thinnest CdTe (0.5 μm) exhibit significantly lower initial efficiency of ~5%, mostly due to the poor fill factor of ~40%. Above 2 μm, some roll-over occurs above ~0.9 V with little change after stress. The curves for 0.75, 1.0, and 1.5 μm CdTe show no roll-over initially but develop a slight roll-over after stressing for forward voltages well above V_{OC} .

CELL STABILITY

The evaporated Cu/Au contact structure used in these cells is known to lead to degraded performance under light soak at open circuit. Diffusion of copper is one mechanism proposed to lead to deterioration of cell performance and the evaporated copper of these contacts might be

expected to show this deterioration most quickly. However, we wanted to test how the CdTe thickness might impact the stability of this contact. The data on stability, shown in Fig. 3 as the open squares, again shows little dependence on CdTe thickness except for the thinnest CdTe (0.5 μm). For these thinnest CdTe structures, the cell efficiency drops to about 50% of its initial value after seven days of stress. The open-circuit voltage and the fill factor make the largest contributions to performance deterioration.

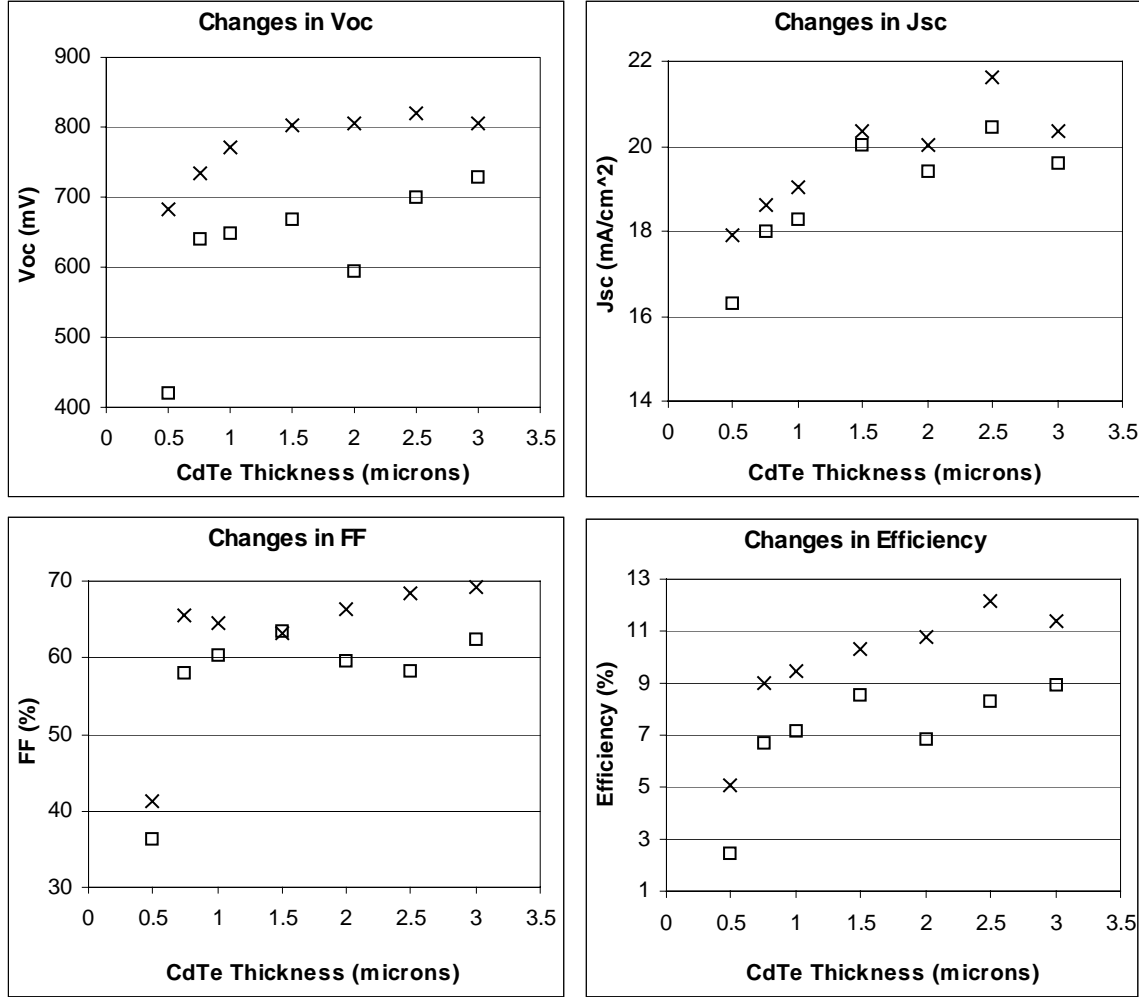


Fig. 3. Changes in cell performance parameters as a function of CdTe thickness. Each data point represents the average of three cells. Symbols are: x = initial values; \square = after light soak at 55 °C for seven days.

CONCLUSIONS

By fabricating a series of CdS/CdTe cells with CdTe thickness from 3.0 μm down to 0.5 μm we have found that the fractional change in cell parameters (V_{OC} , J_{SC} , FF) with stress is independent of thickness down to 0.75 μm . We have kept all the processing conditions constant, as optimized for 2.3 μm CdTe, except for the CdTe thickness and have not made attempts to optimize other processing parameters independently with each CdTe thickness. Therefore we believe that these results could be improved with independent optimization. In particular, were

the CdCl₂ treatment and the back contact process independently optimized, and were an HRT layer used between the tin oxide and the CdS/CdTe, these results would almost certainly improve. We also note that no special care was taken to control Na diffusion although the commercial substrates normally incorporate some diffusion barrier.

Even though these cells used a simple evaporated Cu/Au back contact with no pre- or post-etching, there is little evidence of reduced stability except for 0.5 μm of CdTe. It should be noted that these cells were stressed in wintertime indoor air in Toledo with plenty of available oxygen and significant amounts of water vapor. As reported by Dobson, *et al*, in this Symposium [10] it is possible that these contribute to performance deterioration at all values of CdTe thickness with larger effects at 0.5 μm of CdTe.

From this work, therefore, we judge that there should be no fundamental limit to reducing the CdTe thickness to as little as ~0.75 μm in high efficiency CdTe-based cells. The use of a back reflector could reduce the required CdTe further. This would impact positively on CdTe utilization, potential environmental impacts, and fabrication speed.

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